

LETTER TO THE EDITOR

Ageing, fragility and the reversibility window in bulk alloy glasses

S Chakravarty¹, D G Georgiev¹, P Boolchand¹ and M Micoulaut²¹ Department of Electrical and Computer Engineering and Computer Science, University of Cincinnati, Cincinnati, OH 45221-0030, USA² Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, Boite 121, 4 Place Jussieu, 75252 Paris, Cedex 05, France

E-mail: mmi@lptl.jussieu.fr

Received 3 September 2004, in final form 19 November 2004

Published 10 December 2004

Online at stacks.iop.org/JPhysCM/17/L1**Abstract**

Non-reversing relaxation enthalpies (ΔH_{nr}) at glass transitions $T_g(x)$ in the $P_xGe_xSe_{1-2x}$ ternary display wide, sharp and deep global minima ($\simeq 0$) in the $0.09 < x < 0.145$ range, within which T_g s become *thermally reversing*. In this *reversibility window*, glasses are found *not to age*, in contrast to *ageing* observed for fragile glass compositions outside the *window*. *Thermal reversibility* and *lack of ageing* seem to be paradigms of self-organization which molecular glasses share with *protein* structures which repetitively and reversibly change conformation near T_g and the folding temperature respectively.

Ageing occurs in many materials, both organic and inorganic. Inorganic crystals age under electrical, mechanical, or thermal stresses, often as a result of dislocation motion. Ageing in organic materials is more complex, occurring as hydrogen bonding configurations are altered as a result of thermal cycling. The more complex the system, the less understood are the causes of ageing, and the causes of ageing in living systems are one of the greatest unsolved mysteries in science. Here we will show that inorganic *non-crystalline* nanonetworks are universally divided into three regimes of composition, two of which age rapidly, while the third regime scarcely ages at all. The third regime defines a narrow window of composition that appears to have much in common mechanically with selected organic nanonetworks, namely the polypeptide chains that form proteins. Ageing is not evident in data obtained by conventional structural methods (diffraction, infrared and Raman spectra, magnetic resonance), but it is measured very accurately by modulated differential scanning calorimetry.

New ideas on the nature of glass transitions (T_g) have emerged in recent years from examination [1–3] of the non-reversing relaxation enthalpy (ΔH_{nr}) associated with T_g in temperature modulated differential scanning calorimetry (MDSC) measurements. In MDSC,

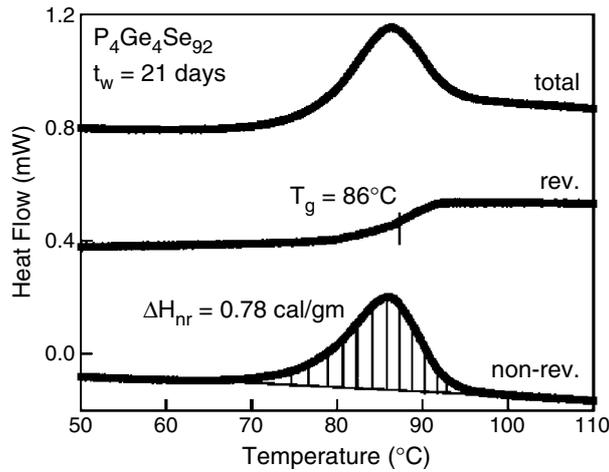


Figure 1. MDSC scan of a $P_4Ge_4Se_{92}$ glass showing the total heat flow deconvoluted into reversing and non-reversing heat flow components. The scan rate was $3\text{ }^\circ\text{C min}^{-1}$ and the modulation rate was $1\text{ }^\circ\text{C}/100\text{ s}$. Note that the T_g from the inflexion point of the reversing heat flow is $86\text{ }^\circ\text{C}$, while the non-reversing enthalpy (shaded area) associated with T_g is 0.78 cal gm^{-1} .

the total heat flow endotherm near T_g can be decomposed into a reversing and a non-reversing component as shown in figure 1. The non-reversing (ΔH_{nr}) endotherm is a signature of ergodicity breaking events when structural arrest of a glass forming liquid occurs near T_g . Examined as a function of mean coordination number, \bar{r} , of network glasses, the endotherm (ΔH_{nr}) is found to nearly vanish [1–5] across *compositional windows*, $\bar{r}_c(1) < \bar{r} < \bar{r}_c(2)$, wherein glass transitions become *thermally reversing* in character. Furthermore, these reversibility windows are found to be closely related to variations in Raman optical elasticities [3–5]. Distinct elastic power-laws are seen in at least two composition regimes: $\bar{r}_c(1) < \bar{r} < \bar{r}_c(2)$ (the window), and above $\bar{r} > \bar{r}_c(2)$ [3–5]. Theoretical support for the existence of these elastic phases comes from several related considerations, namely, the counting of Lagrangian constraints [6], graph theory [7] and numerical simulations [7, 8]. From these considerations Phillips and Thorpe have identified [6–8] the existence of three generic elastic phases as a function of \bar{r} : floppy, intermediate and stressed rigid. Thus, $r_c(1)$ and $r_c(2)$ mark the onset and end of the reversibility window, and are the two phase boundaries between these three elastic phases. Intermediate phases are generally centred on mean coordination numbers close to 2.40, and are thought to consist of isostatic (rigid but unstressed) structures. In the present work we examine the rates of network ageing in the three composition regimes as measured by changes in the kinetics of the glass transition in samples relaxed at room temperature (far below the glass transition temperatures) over several months. Our results show that strain plays an important part in network ageing, and that the absence of long-range strains is a necessary condition for non-ageing.

Intuitively one might anticipate non-ageing in the very stable and self-organized structure that could exist between the two less stable structure regimes, namely floppy structures with polymer chain entanglements frozen upon quenching and overconstrained stressed-rigid structures with locked-in extra bonds on the other. The caveat, however, is the possible presence of nanoscale phase separation which invalidates mean field constraint counting particularly in the would be optimally constrained phase. Such separation often occurs in binary selenides, $(T\text{ or Pn})_x\text{Se}_{1-x}$, where T is a tathogen (Si, Ge) and Pn a pnictide (P, As), and manifests itself

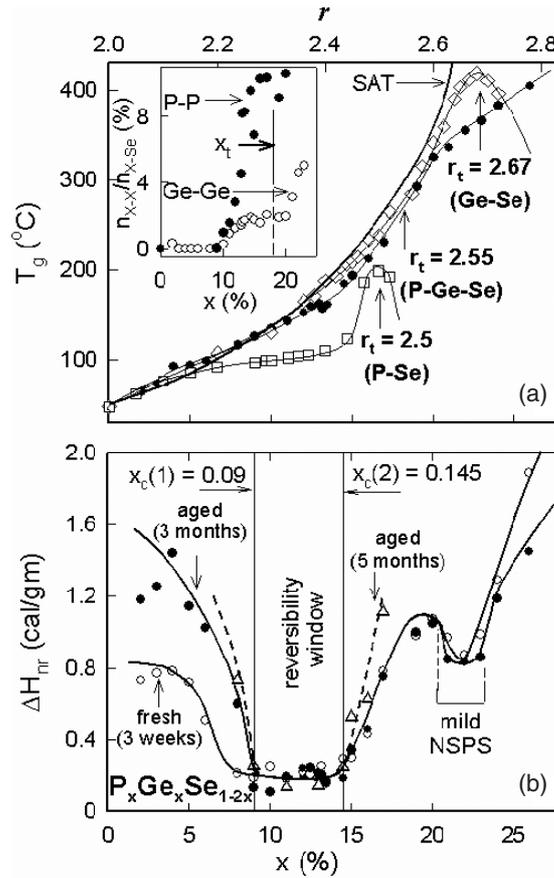


Figure 2. (a) $T_g(\bar{r})$ trends in Ge–Se (\diamond), P–Se (\square) and P–Ge–Se (\bullet) glasses. The thick black curve shows the $T_g(\bar{r})$ prediction [10, 11] based on SAT. The inset shows the concentration of homopolar bonds projected by stochastic agglomeration theory to account for the observed $T_g(\bar{r})$ trend. The x -axis scale for the inset is the same as that of the ternary in figure 1(a). (b) Trends in $\Delta H_{nr}(x)$ in the $\text{Ge}_x\text{P}_x\text{Se}_{1-2x}$ ternary showing the reversibility window in the $0.09 < x < 0.145$; the latter gets deeper and sharper upon ageing of glass samples at 300 K.

in global maxima of $T_g(x)$ near chemical thresholds [10, 11] (figure 2(a)). However, in ternary selenides, $\text{T}_x\text{Pn}_x\text{Se}_{1-x}$, containing equal fractions of T and Pn atoms, these global maxima are conspicuously absent [12], and $T_g(x)$ is found to increase monotonically with x , as illustrated for the case of T = Ge, Pn = P ternary in figure 2(a). In this letter, we identify the reversibility window ($0.09 < x < 0.145$) in the $\text{P}_x\text{Ge}_x\text{Se}_{1-2x}$ ternary and find it to be wide, sharp and deep. Furthermore, glasses in the window are found not to age, in sharp contrast to ageing observed for glass compositions outside the window. Thermal reversibility and absence of ageing appear to be common features of both glasses in reversibility windows and proteins in folding states [13, 14], and are connected with self-organization effects of these disordered networks.

Our dry, homogenized samples were prepared as described previously [3]. Glass transition temperatures, $T_g(x)$, and non-reversing relaxation enthalpy, $\Delta H_{nr}(x)$, were established using a model 2920 MDSC from TA Instruments. Measurements were performed on fresh (3 weeks) and aged (3 and 5 months) samples relaxed at 300 K. We find $T_g(x)$ to increase monotonically

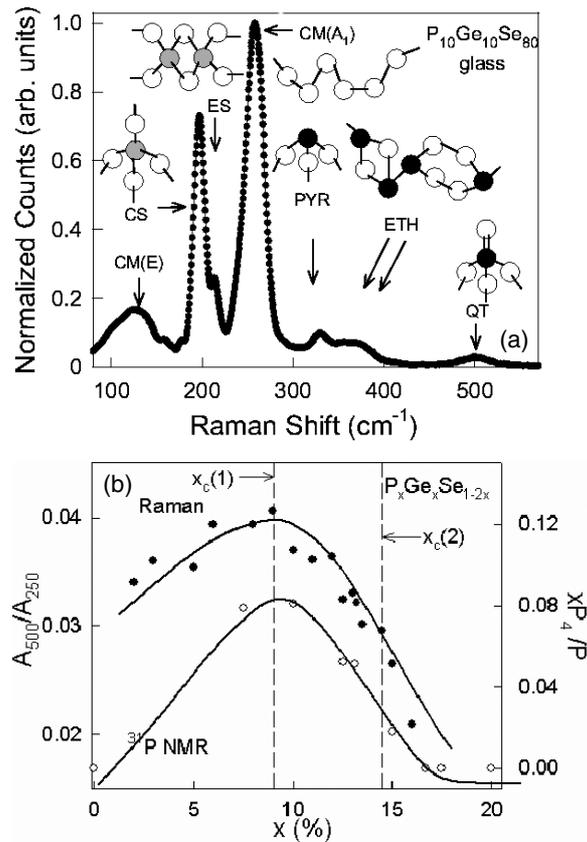


Figure 3. (a) Raman scattering of a ternary $P_x Ge_x Se_{1-2x}$ glass at $x = 0.10$ showing modes [15–21] of quasi-tetrahedral (QT) units (500 cm^{-1}), ethylene-like (ETH) $P_2 Se_3$ units (375 cm^{-1}), pyramidal (PYR) $P(Se_{1/2})_3$ units (330 cm^{-1}), Se_n chain mode (CM) at 250 and 140 cm^{-1} , corner-sharing (CS) and edge-sharing ES $Ge(Se_{1/2})_4$ units near 200 and 217 cm^{-1} respectively [17]. (b) Shows a plot of the Raman scattering strength of the QT mode normalized to the CM at 250 cm^{-1} in open circles, while the filled circles give concentrations of the QT units inferred from ^{31}P NMR, [21].

with x in the $0 < x < 0.25$ range (figure 2(a)). Variations in $\Delta H_{nr}(x)$ show (figure 2(b)) a global minimum in the $0.09 < x < 0.145$ range that becomes relatively sharper and deeper as the glasses outside the window age. In the $0.20 < x < 0.23$ range, variations in $T_g(x)$ and $\Delta H_{nr}(x)$ show a mild glitch (figure 2(a)) and a satellite window (figure 2(b)) respectively. Raman scattering on glasses excited in the IR ($1.06\text{ }\mu\text{m}$) were performed in a back scattering geometry using a Nicolet FT Raman module with model 870 FTIR bench at 1 cm^{-1} resolution. Fourteen bands were identified and their strengths traced as functions of composition in order to monitor the nature of the molecular clusters and the degree of nanoscale phase separation. This allows the identification (figure 3(a)) of P-centred [15–18] pyramidal (PYR) and quasi-tetrahedral (QT), and Ge-centred [5, 19, 20] corner-sharing (CS) and edge-sharing (ES) units from their vibrational modes. The nature of the P-centred units is independently confirmed from P^{31} NMR results [21]. These considerations led to the construction of a full ternary phase diagram showing the regimes of the three generic elastic phases observed near the stiffness transition in these alloys; details will be published elsewhere. The molar volumes of the glasses in the fresh and aged state were measured (figure 4) using Archimedes' method.

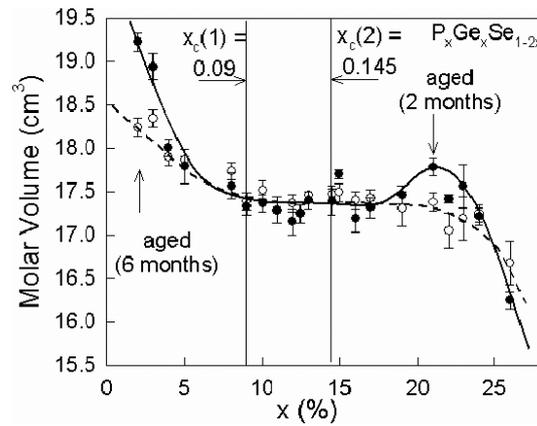


Figure 4. Molar volumes of present glasses measured 2 months (●) and 6 months (○) after water quench. Note that ageing effects occur for glass compositions outside the reversibility window but not inside the window.

Table 1. Onset \bar{r}_1 and end \bar{r}_2 of intermediate phases observed in indicated binary and ternary network glasses and proteins.

| Network | Intermediate phase | | Reference |
|----------|--------------------|-------------|-----------|
| | \bar{r}_1 | \bar{r}_2 | |
| Ge–Se | 2.40 | 2.52 | [20] |
| Si–Se | 2.40 | 2.53 | [4] |
| As–Se | 2.29 | 2.37 | [1] |
| P–Se | 2.28 | 2.40 | [17] |
| Ge–S–I | 2.332 | 2.342 | [25] |
| P–Ge–Se | 2.27 | 2.43 | Present |
| Proteins | 2.39 | 2.42 | [13] |

The central result of the present work is the observation of a deep and wide reversibility window in the $0.09 < x < 0.145$ (or $2.27 < \bar{r} < 2.44$) range (table 1). The window delineates the three elastic phases: floppy at $\bar{r} < 2.27$, intermediate in the $2.27 < \bar{r} < 2.44$ range, and stressed rigid at $\bar{r} > 2.44$. Here $\bar{r} = 2 + 3x$ [2]. The reversibility window sharpens and gets deeper as glass compositions outside the window age at 300 K (figure 1(b)). Floppy glasses (below the window) age over a 3 month waiting period, while stressed-rigid glasses (above the window) age somewhat slower, over ≈ 5 months. The slower ageing kinetics of the latter phase is probably connected with their higher T_g s. There is no evidence of ageing for glasses in the reversibility window even after a 5 month waiting period. Since the lack of ageing in the reversibility window is inferred from the $\Delta H_{nr}(x)$ term, the aged samples could not be crystalline since they display a glass transition.

In the reversibility window composition range the local structures are thought to consist of CS ($\bar{r} = 2.40$ – 2.67) and ES ($\bar{r} = 2.67$) $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra, pyramidal ($\bar{r} = 2.40$) $\text{P}(\text{Se}_{1/2})_3$ and quasi-tetrahedral ($\bar{r} = 2.28$) $\text{Se} = \text{P}(\text{Se}_{1/2})_3$ units. These structural units all have the feature [2] that the number of Lagrangian constraints/atom due to bond-stretching and bond-bending forces equals 3, the degrees of freedom/atom according to which they comprise isostatic rigidity [7, 8]. The exceptional thermal and elastic behaviour of glasses in the reversibility window derives from the isostatically rigid nature of their backbones. From

theoretical considerations it is plausible that the backbones of these alloys can be made up entirely of such isostatic units over the range of the reversibility window [2, 3, 5, 9, 22]. Thus, for example, the window begins near $\bar{r} = 2.28$ where the concentration of QT units ($\bar{r} = 2.28$) maximizes [21] (figure 3(b)), and the window ends near $\bar{r} = 2.44$ where the concentrations of PYR units ($\bar{r} = 2.40$), CS ($\bar{r} = 2.40$ – 2.67) and ES units ($\bar{r} = 2.67$) are high (figure 2(a)). Furthermore, one would expect molecular packing of these units as manifested in molar volumes of the glasses to show absence of ageing effects as is indeed observed (figure 4) for window compositions. In the latter, the molar volumes are compact and they are found to be nearly independent of coordination number. Recently a reversibility window analogue in densified silica has been identified [23] in molar volumes examined as a function of pressure at high temperatures.

MDSC and Raman scattering on $P_x\text{Ge}_x\text{Se}_{1-2x}$ glasses have permitted the isolation of the reversibility window and analysis of its average and local structures. One of the popular qualitative descriptions of glasses uses the temperature dependence of the viscosity of a supercooled melt in terms of whether it exhibits a constant Arrhenius activation energy, or whether this energy increases as the melt is supercooled; the former materials are said to form strong glasses, the latter fragile ones [24]. In $\text{As}_x\text{Se}_{1-x}$ binary glasses we have already pointed out that the reversibility window ($0.30 < x < 0.37$) coincides with a window ($0.28 < x < 0.36$) in activation energies for viscosity relaxation [3]. Here the activation energy E_η for viscosity relaxation is established by measuring the slope $d(\ln \eta)/d(1/k_B T)$. The global minimum in $E_\eta(x)$ that coincides with a global minimum in ΔH_{nr} suggests that strong liquids give rise to glasses in the intermediate phase. The essential new feature here is the evidence that for the same composition range there does not seem to be structural ageing, in sharp contrast to the behaviour encountered for fragile glass compositions outside this window.

The two features of reversible melting and structural non-ageing seen in the present work in the compositional window in glasses (intermediate or self-organized phase) are most suggestive of a correspondence with the protein folding transition. DSC measurements on a variety of proteins show that the unfolding (denaturation) process is thermodynamically reversible and reproducible over the several scan cycles examined in DSC experiments [26]. Of course, protein functionality demands that there be almost no ageing and nearly complete reversibility.

A structural correspondence between the folding/unfolding critical state of proteins and the self-organized phase of glasses is also strongly suggested by recent numerical studies of the rigidity transition in skeletal models of functional polypeptide chains of proteins [13]. For 26 protein structures a mechanical stiffness transition upon denaturation is found when the average coordination number \bar{r} is 2.41, close to the value for glasses. These ideas lend credence to the notion of similarity in function between glasses and proteins that was recognized earlier [27] in a more general fashion. Further investigations of the similarities and differences in the mechanical behaviour of proteins near denaturation and self-organized glasses are in order.

We thank M Mabry and B Zuk of ThermoNicolet Inc. for the Raman measurements and B Goodman and J C Phillips for discussions during the course of this work. LPTL is Unite Mixte de Recherche CNRS No 7600. This work is supported by NSF grant DMR-01-01808.

References

- [1] Georgiev D G, Boolchand P and Micoulaut M 2000 *Phys. Rev. B* **62** R9228
- [2] Wang Y, Boolchand P and Micoulaut M 2000 *Europhys. Lett.* **52** 633
- [3] Boolchand P, Georgiev D G and Micoulaut M 2002 *J. Optoelectron. Adv. Mater.* **4** 823
see also: Boolchand P, Georgiev D G and Micoulaut M 2001 *J. Optoelectron. Adv. Mater.* **3** 703
- [4] Selvanathan D, Bresser W J and Boolchand P 2000 *Phys. Rev. B* **61** 15061

-
- [5] Qu T, Georgiev D G, Boolchand P and Micoulaut M 2003 *Supercooled Liquids, Glass Transition and Bulk Metallic Glasses (Mater. Res. Soc. Symp. Proc. vol 754)* ed T Egami, A L Greer, A Inoue and S Ranganathan (Warrendale, PA: Materials Research Society) p 111
- [6] Phillips J C 1979 *J. Non-Cryst. Solids* **34** 153
- [7] Thorpe M F, Jacobs D J, Chubinsky N V and Rader A J 1999 *Rigidity Theory and Applications* ed M F Thorpe and P M Duxbury (New York: Academic) p 239
- [8] Thorpe M F, Jacobs D J, Chubynski M V and Phillips J C 2000 *J. Non-Cryst. Solids* **266–269** 859
- [9] Phillips J C 2002 *Phys. Rev. Lett.* **88** 216401
- [10] Kerner R and Micoulaut M 1997 *J. Non-Cryst. Solids* **210** 298
- [11] Micoulaut M 1998 *Eur. Phys. J. B* **1** 277
- [12] Boolchand P, Georgiev D G, Qu T, Wang F, Cai L and Chakravarty S 2002 *C. R. Chimie* **5** 713
- [13] Rader A J, Hespenheide B M, Kuhn L A and Thorpe M F 2002 *Proc. Natl Acad. Sci. USA* **99** 3540
Thorpe M F 2003 *APS News* **2** 10
- [14] Fersht A 1999 *Structure and Mechanism in Protein Science: A Guide to Enzyme Catalysis and Protein Folding* (New York: Freeman)
- [15] Bues W, Somer M and Brockner W 1980 *Z. Naturf.* b **35** 1063
- [16] Andreas K, Alexander K and Martin T 2002 *J. Chem. Phys.* **116** 3323
- [17] Georgiev D G, Mitkova M, Boolchand P, Brunklaus G, Eckert H and Micoulaut M 2001 *Phys. Rev. B* **64** 134204
- [18] Jackson K, Briley A, Grossman S, Porezag D V and Pederson M R 2001 *Phys. Rev. B* **60** R14985
- [19] Murase K 2000 *Insulating and Semiconducting Glasses* ed P Boolchand (Singapore: World Scientific) p 415
- [20] Feng X, Bresser W J and Boolchand P 1997 *Phys. Rev. Lett.* **78** 4422
- [21] Lyda C, Tepe T, Tullius M, Lathrop D and Eckert H 1994 *J. Non-Cryst. Solids* **171** 271
- [22] Micoulaut M and Phillips J C 2003 *Phys. Rev. B* **67** 104204
- [23] Trachenko K and Dove M T 2003 *Phys. Rev. B* **67** 212203
- [24] Angell C A 1988 *J. Non-Cryst. Solids* **102** 205
Angell C A 1991 *J. Non-Cryst. Solids* **131–133** 13
- [25] Wang Y, Wells J, Georgiev D G, Boolchand P, Jackson K and Micoulaut M 2001 *Phys. Rev. Lett.* **87** 185503
- [26] Privalov P L 1997 *J. Chem. Thermodyn.* **29** 447
- [27] Fraunfelder H, Wolynes P G and Austin R H 1999 *Rev. Mod. Phys.* **71** S419